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Accumulation of polycyclic aromatic hydrocarbons by lichen transplants: Comparison with gas-phase passive air samplers

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HIGHLIGHTS

- Concentrations of PAHs in lichens reflected atmospheric concentrations.
- An exposure of 3 months allowed reaching equilibrium between lichens and air.
- Lichens provide quantitative information on the load by PAHs in the atmosphere.
- Lichen values may be translated into atmospheric concentrations.

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ABSTRACT

This study compared the accumulation of 16 polycyclic aromatic hydrocarbons (PAHs) in samples of the lichen *Evernia prunastri* exposed for 3 months in and around an industrial area of S Italy with that in co-located passive gas-phase air samplers. The results showed a strong linear correlations ($R = 0.96$, $P < 0.05$) between total PAHs in lichens and in passive samplers, clearly indicating that lichen transplants may provide direct quantitative information on the atmospheric load by total PAHs, allowing translation of lichen values into atmospheric concentrations. To the best of our knowledge this is the first study reporting such a correlation with gas-phase passive air samplers.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a wide class of chemical compounds composed of carbon and hydrogen atoms forming fused aromatic rings. They are pollutants that may originate from both natural and anthropogenic sources, but the latter are largely dominant, being mostly formed during incomplete combustion of fossil fuels and organic matter, and evaporation of petroleum derivatives (Ravindra et al., 2008).

In recent years atmospheric PAHs have been thoroughly investigated since some of them, notably benzo[*a*]pyrene, have been recognized as carcinogenic and mutagenic (Bostrom et al., 2002), and 16 of them have been classified as priority pollutants by the US EPA (2003). Moreover, owing to their mobility, persistence in the environment, ability to accumulate in the biota and toxicity to humans, PAHs have been included in the Convention on Long Range Transboundary Air Pollution Protocol (CLRTAP) on Persistent Organic Pollutants (EMEP, 2014).

After emission in the atmosphere, the most volatile PAHs, i.e. those with low molecular weight (2–3 rings), usually remain in the gas-phase, while PAHs with high boiling points, i.e. those with high molecular weight (5–6 rings), are adsorbed on solid particulate matter; PAHs with 4 rings have an intermediate behavior (Edwards, 1983).

The use of plants as bioindicators has proved very useful for the evaluation of atmospheric levels of PAHs (Thomas et al., 1984; Migaszewski et al., 2002) and lichens emerged as particularly suitable for this purpose (Schrlau et al., 2011; Studabacker et al., 2012). A good agreement has been reported for PAHs profile in lichens and atmospheric particulate (Blasco et al., 2006; Augusto et al., 2010), while less clear relationships were found for gas-phase PAHs (Schrlau et al., 2011; Studabacker et al., 2012). However, a characteristic of these studies is that they all used data from native

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(*in situ*) lichens, thus preventing a direct quantitative comparison of lichen data with conventional data from air samplers, owing to the differences in exposure time. This problem may be circumvented by using lichen samples collected from a remote site and transplanted into the area to be monitored, thus allowing for initial conditions and exposure time being known (Paoli et al., 2011).

The aim of this study was to compare the accumulation and profile of PAHs in transplanted lichens with those in co-located passive gas-phase samplers. To the best of our knowledge this is the first study specifically designed to compare PAHs in lichen transplants and passive air samplers.

2. Materials and methods

2.1. Study area

Lichen transplants and passive air samplers were exposed together for 3 months (April 12–July 21, 2011) at 10 sites in and around an industrial area of S Italy (14°4′–14°9′E and 31°29′–31°32′N Grw, Molise region, elevation 200–900 m asl, annual precipitation 700 mm, mean annual temperature 14 °C) concerned by activities such as manufacturing and processing of metals, chemicals, plastics, electronics, agri-food stuff and a municipal solid waste incinerator.

2.2. Lichen transplants

Samples of the fruticose (shrub-like) lichen *Evernia prunastri* L. (Ach.) were collected at a remote site of Molise and transplanted (10 thalli per site) into the study area at ca. 2 m above the ground on local trees, ensuring exposure conditions similar to those in their natural habitat.

E. prunastri was chosen since this lichen is easy to collect, transplant and prepare for the analysis and has a high surface/volume ratio to intercept airborne pollutants (Ayrault et al., 2007). It grows abundantly in the study area and was previously used for monitoring purposes in the same region (Paoli et al., 2011). Moreover, a comparative study on the behavior of different lichen species as biomonitors of air pollution by PAHs showed that *E. prunastri* is the most appropriate, providing information both on pyrogenic and petrogenic PAHs (Blasco et al., 2011).

2.3. Passive samplers

Passive air samplers have the advantage that can be deployed at sampling sites without the need for electricity, which is instead required for operating active high-volume air samplers. Polyurethane foam (PUF) samplers were used since they provide a quantitative measure of gas-phase PAHs present in the air (Lane, 1999) and are employed worldwide in the study of air pollution by persistent organic pollutants (Harner et al., 2006). Details of PUF functioning can be found in Estellano et al. (2012, 2014). In brief, PUF samplers consisted of PUF disks with the following characteristics: diameter, 14 cm; thickness, 1.35 cm; surface area 365 cm^2; mass, 4.4 g; volume, 207 cm^3; density, 0.0213 g cm^{-3} (PacWill Environmental, Stoney Creek, ON). PUF disks were housed inside a stainless steel chamber consisting of two stainless steel domes with external diameters of 30 cm and 20 cm.

2.4. Chemical analysis

Lichen samples (ca. 2 g each) were extracted by Soxhlet for 24 h using 300 mL of n-hexane as solvent. The extract was cleaned up in a column with silica (2 g) and Na_2SO_4 (0.5 g) and subsequently the purified extract was concentrated to 1 mL with a Rotavapor (Buchi) and solvent exchanged to 0.5 mL of isooctane. The same procedure was used for PUF samplers, using petroleum ether instead of n-hexane and skipping the clean up phase.

The 16 USEPA PAHs, namely naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a,h*]anthracene, benzo[*ghi*]perylene, indeno[*1,2,3-cd*]pyrene were determined and quantified by GC–MS (ion trap detector, ThermoFinnigan Trace™ GC 2000/GCQ plus) equipped with a Restek Rtx-5 MS (30 m × 0.25 mm × 0.25 μm ID) capillary column, using helium as carrier gas at 1 mL min^{-1} constant flow. The injection in the GC system was run in spitless mode, with spitless time 5 min and injector temperature 250 °C. The GC oven temperature was held at 100 °C for 2 min, increased of 20 °C min^{-1} for 10 min to 140 °C, than increased again of 4 °C min^{-1} for 13 min to 200 °C and of 4 °C min^{-1} for 10 min to 300 °C. The transferline temperature was 280 °C and the El+ source temperature 200 °C; filament energy was 70 eV. Recoveries were checked by spiking a portion of samples prior to extraction and analysis with phenanthrene-d_{10} (99%, Cambridge Isotope Laboratory) and were found to be 85 ± 10%.

Concentrations were expressed on a dry weight (dw) basis for lichens (ng g^{-1}) and on a volume basis (ng m^{-3}) for passive samplers, the latter calculated considering the air volume sampled during the exposure period (see Estellano et al., 2012 for details on derived air sample volumes).

2.5. Statistical analysis

For the calculations, data below the limit of quantification (LOQ) were assumed to be LOQ/2 (Menichini and Viviano, 2004). Owing to the limited dataset non parametric statistics were used. Correlations between lichen data and passive samplers data were tried with the Spearman correlation coefficient.

3. Results

At the end of the exposure period, it was found that the passive samplers at 3 of 10 stations were missing and assumed to be removed by vandals. Thus, the results and analysis presented below refer to only 7 stations.

3.1. Lichen transplants

Concentrations (ng g^{-1} dw) of individual and total PAHs measured in lichen transplants exposed for 3 months in the study area are reported in Table 1. The analysis allowed the detection of 6 out of the 16 US-EPA PAHs investigated (acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene), but quantification was not possible for acenaphthene. Concentrations of

Table 1
Concentrations (ng g^{-1} dw) of individual and total PAHs in lichen transplants. Acy = acenaphthylene, Ace = acenaphthene, Flu = fluorene, Phe = phenanthrene, Flt = fluoranthene, Pyr = pyrene, PAHs = total PAHs; LOQ = limit of quantification.

Station	Acy	Ace	Flu	Phe	Flt	Pyr	PAHs
1	8	<LOQ	94	68	57	77	304.5
2	<LOQ	<LOQ	2	117	2	2	124
3	<LOQ	<LOQ	1	16	<LOQ	2	20.9
4	<LOQ	<LOQ	1	12	2	3	19
5	<LOQ	<LOQ	10	344	175	129	659
6	<LOQ	<LOQ	11	400	177	<LOQ	589.5
7	2	<LOQ	48	371	119	142	682.5
LOQ	0.9	0.9	0.7	1	1.8	1	

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